

Resonance Revisited: A Consideration of the Calculation of Cyclic Conjugation Energies

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ABSTRACT

A homomolecular differential bond separation reaction may be defined as the difference between the conventional bond separation reactions involving the unsaturated system and its saturated counterpart. Such a reaction is homomolecular in that the basic molecular structures involved are the same on both sides of the reaction. The type of homodesmotic reaction that also conserves structure in this way may be termed a homomolecular homodesmotic reaction. Both types of homomolecular reactions are readily related to hydrogenation reactions and, more importantly, to each other. $\Delta B(n)$, the energy of the homomolecular differential bond separation reaction involving a system with n double bonds, and $H(n)$, the corresponding homomolecular homodesmotic reaction, are related by:

$$\Delta B(n) - H(n) = n \cdot (h(1) - h(e))$$

where $h(1)$ and $h(e)$ are the hydrogenation energies of the system's monoene and of ethylene, respectively. Both types of reactions yield measures of cyclic conjugation energies that for certain classifications of molecules are simply related to each other. Consideration of extra conjugation in the monoenes allows a ready interpretation of those cases in which a simple classification is not obtained. *Ab initio* calculations illustrating these effects have been carried out on a variety of molecules including many five- and six-membered ring systems using second order Møller–Plesset and density functional approaches. © 1997 by John Wiley & Sons, Inc.

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Introduction

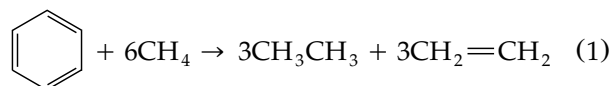
The idea of resonance and resonance energy is an old and fundamental concept in chemistry dating back to Pauling's discussion of the idea of resonance among valence bond structures leading to an extramolecular stability.¹ It is a concept that is considered very important in organic chemistry when one talks about cyclic conjugation stability, or aromaticity, a topic that has recently been reviewed in the book by Minkin et al.² Resonance was discussed extensively in the classic text of Wheland³ published in 1955 where extensive tables of resonance energies are given based on heats of formation and heats of hydrogenation.

While it is a powerful qualitative concept, the quantification of cyclic conjugation stability has proven to be remarkably elusive. A number of approaches involving energy changes in realizable chemical reactions have been proposed to define it, each of which provides a measure of aromaticity (cyclic conjugation), although the resulting numbers differ because of the differing definitions. The two probably best known are the isodesmic bond separation reaction of Hehre et al.^{4,5} and the ring-preserving homodesmotic reaction of George et al.⁶ (*vide infra*). In the present work we have carried out *ab initio* energy calculations for both ring-preserving homodesmotic and modified bond separation reactions for a variety of five- and six-membered rings as well as some other illustrative systems. We compare these two approaches to the estimation of cyclic resonance energies and demonstrate the relationship between them that exists through their hydrogenation reactions. Both conventional *ab initio* second order Møller–Plesset⁷ as well as density functional calculations have been carried out.

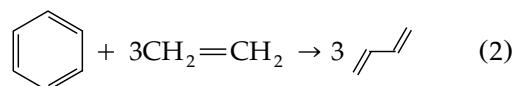
Cyclic Stability Energies from Chemical Reactions

Hehre et al. introduced the idea of *isodesmic* bond separation reactions in 1970.^{4,5} They coined the term *isodesmic* that implies a transformation (chemical reaction) in which the number of bonds of each formal type are conserved and only the relationships among them are altered. In a bond separation reaction all formal bonds between non-hydrogen atoms are separated into the simplest

two-heavy-atom parent molecules containing the same kind of linkages. Stoichiometric balance is obtained by the addition of mono-heavy-atom hydrides to the equation; the example of benzene is shown in eq. (1). A desirable aspect of this particular way of measuring extramolecular stability or resonance energy is its simplicity and the fact that a unique bond separation reaction may be written for any molecule in which a unique classical valence structure may be drawn.⁸ On the other hand, it suffers from the need to involve simple hydrides that do not involve bonds between heavy atoms. Thus, physically, one breaks CH bonds in methane but forms CH bonds in ethane and ethylene (and other species in heteronuclear rings). These CH bond energies differ significantly, and because a large number of methanes must be added to a reaction, the “noise” level of the energy involved taken as representing the resonance energy is increased.

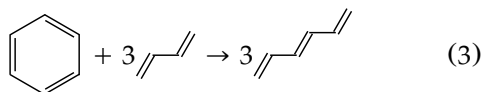


George and coworkers modified Pople's bond separation reaction to what they called a *homodesmotic* reaction.⁹ They define a homodesmotic reaction as one in which there are equal numbers of carbon atoms in their various states of hybridization in reactants and products, and also where there is a matching of carbon—hydrogen bonds in terms of the number of hydrogen atoms joined to individual carbon atoms in reactants and products; the case of benzene is again illustrated in eq. (2). As this definition implies, George et al.⁹ were basically interested in aromatic stabilization energies in purely carbon-containing compounds. In this type of homodesmotic reaction, stoichiometric balance is obtained with the addition of ethylene, the prototypical carbon—carbon double bond system. The homodesmotic reaction is an improvement in one sense over the isodesmic bond separation reaction in that energy contributions due to changes in hybridization of carbon atoms in reactants and products are eliminated, and energy contributions due to changes in the nature of carbon—hydrogen bonds in reactants and products are minimized.

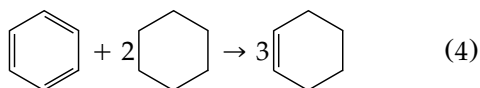


Nyulászai and coworkers^{10,11} in their study of five-membered rings have introduced the idea of a *semihomodesmotic* reaction, which is a kind of combination of a bond separation reaction and a proper homodesmotic reaction. They note that the semihomodesmotic reaction is not truly homodesmotic, but does compare the stability of the ring to systems with four π electrons and, in this regard, is analogous to the homodesmotic reaction written for six-membered rings. In their recent study on the aromaticity of five-membered heterocycles, they conclude that it, along with the normal homodesmotic reaction, provides a good description of aromaticity.

An extension of the homodesmotic reaction to what is called the *hyperhomodesmotic* (or *superhomodesmotic*) reaction was suggested by Hess and Schaad.¹² Here there is a further, more detailed definition of bond types to be conserved, and the reactions become more complicated, as shown for benzene in eq. (3). A large number eight of multiply-bonded carbons are classified by Hess and Schaad according to the number of hydrogens attached to each carbon atom. The hyperhomodesmotic reaction is a subclass of the homodesmotic reaction which is itself a subclass of the isodesmic reaction.

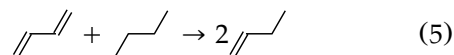


George et al.⁶ point out what we believe to be a more appropriate type of homodesmotic reaction involving ring systems, namely that where one compares the unsaturated species with its cyclic monoene, a procedure evidently first used by Kistiakowsky and coworkers in their formulation of the resonance energy of benzene¹³ comparing its heat of hydrogenation to that of cyclohexene.¹⁴ Schleyer et al.¹⁵ have recently carried out *ab initio* calculations on some five-membered rings using this approach. With this method the conjugated ring with multiple double bonds is converted to the corresponding cyclic monoene, and the equation is balanced through the addition of the completely saturated analog of the conjugated system; eq. (4) provides an example. Note that, because the

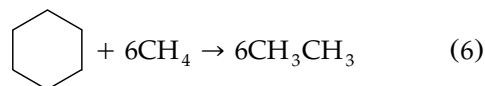


reference compounds are all computed in their most stable conformations, strain effects will tend to cancel to a large extent. This definition of ho-

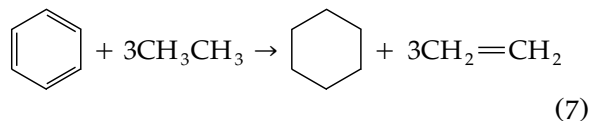
modesmotic reactions for cyclic systems is straightforward and can be generalized. We refer to this type of reaction as a *homomolecular* homodesmotic reaction because similar molecular frameworks are employed to characterize the resonance effect.¹⁶ It can be applied not only to ring systems but also to noncyclic structures as well as illustrated by *trans*-butadiene below.



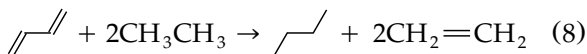
Just as the homomolecular homodesmotic reactions [eqs. (4) and (5)] would seem to be an improvement over the earlier version [eq. (2)], the simple bond separation approach illustrated in eq. (1) can be made homomolecular by comparing the *difference* in bond separation energies of the related unsaturated and saturated ring systems, which we propose calling a homomolecular *differential* bond separation reaction. This approach basically involves comparing double bonds in a ring to ethylenic double bonds and was illustrated in the work of George et al.⁶ who cite Dewar and Schmeising¹⁷ as first mentioning it. The idea has also been pointed out by Simkin et al.¹⁸ in a recent review article. Again, using benzene as an example, one would evaluate the energy associated with the fully saturated species [eq. (6)]



and then take the difference of reactions in eqs. (1) and (6) to obtain



In eq. (7) we see that the double bonds in the ring are now compared to double bonds in (prototypical) ethylene, and it is no longer necessary to consider the mono-heavy-atom hydrides as reaction reagents. This reaction is homomolecular in that similar molecular frameworks are used to measure the resonance effect and it is clear that this is another, natural way of looking at the effect of ring conjugation. As with the previous modified homodesmotic reaction, this approach can also be applied to noncyclic systems, as shown for *trans*-butadiene in eq. (8)

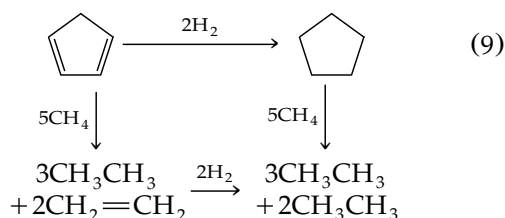


Equivalence to Hydrogenation Reactions

Early in the study of resonance effects, one of the more accurate determinations of resonance energies in cyclic organic systems and what could be called the "classical" approach involved the use of hydrogenation energies,³ as illustrated in the work of Kistiakowski et al.^{13,14} who compared the hydrogenation energy of benzene to three times the hydrogenation energy of cyclohexene. Heats of formation of "normal" molecules were also used to determine additivity schemes for molecular fragments from which one could estimate the extra stabilization energy seen in conjugated systems. But the drawback to this latter approach is that these reactions do not relate directly to any that can be carried out in the laboratory. Heats of hydrogenation obviously do, as do the reactions illustrated above including the homomolecular homodesmotic and bond separation reactions.

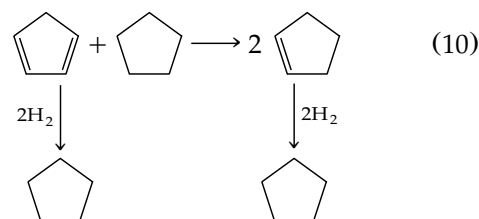
The two homomolecular reactions just discussed are both equivalent to simple heats of hydrogenation approaches. We illustrate this equivalence for cyclopentadiene and the related molecules cyclopentene and cyclopentane. First, we denote the bond separation reaction energy for a species with n double bonds as $B(n)$, its hydrogenation energy by $h(n)$, and let $H(n)$ represent the homomolecular homodesmotic reaction energy; the homomolecular differential bond separation reaction energy is then defined by $\Delta B(n) \equiv B(n) - B(0)$.

Consider first the sequence of reactions shown in eq. (9) containing bond separation reactions. It is clear that $h(2) + B(0) = B(2) + 2h(e)$, where $h(e)$ represents the hydrogenation energy of ethylene; that is, $B(2) - B(0) = \Delta B(2) = h(2) - 2h(e)$, and the homomolecular differential bond separation reaction energy is a simple difference of hydrogenation energies.



Consider next the sequence of reactions in eq. (10) where a homodesmotic reaction is involved. Here it is clear that $H(2) + 2h(1) = h(2)$, or $H(2)$

$= h(2) - 2h(1)$, and the homomolecular homodesmotic reaction energy is also related to a simple difference of hydrogenation energies. As mentioned previously, this particular approach is precisely the classical approach involving hydrogenation energies used many years ago.^{3,13}



One can easily generalize to the case of systems with n double bonds. Then,

$$\Delta B(n) = h(n) - n \cdot h(e) \quad (11)$$

$$H(n) = h(n) - n \cdot h(1) \quad (12)$$

so that

$$\Delta B(n) - H(n) = n \cdot [h(1) - h(e)] \quad (13)$$

which shows that the energy difference between a homomolecular differential bond separation reaction and the corresponding homodesmotic reaction is simply related to the difference between the hydrogenation energy of the monoene and ethylene times the number of formal double bonds involved.

This difference is not small for cyclic monoenes. Consider the heats of formation data of Pedley et al.¹⁹ from which hydrogenation ΔH values may be calculated. Assuming that translational and rotational degrees of freedom each contribute $\frac{1}{2}RT$ to the energy, the difference between ΔH and ΔE_{elect} (the electronic energy difference expressed above, and which we calculate later) values for the hydrogenation reactions is equal to the difference between zero-point energy differences in the monoene and ethylene hydrogenations. Neglecting this difference for the moment, the experimental ΔH data then provide an *estimate* of the quantity of interest. The ΔH value for ethylene is -32.6 kcal/mol and the higher linear 1-monoenes exhibit essentially constant values of -29.9 kcal/mol. The cyclic systems, however, show larger differences. For the cyclic monoenes containing N carbon atoms, the values are -30.7 ($N = 4$), -26.4 ($N = 5$), -28.3 ($N = 6$), -26.0 ($N = 7$), and -23.3 ($N = 8$); this gives rise to $h(1) - h(e)$ ΔH values of 1.9, 6.2, 4.3, 6.6, and 9.3 kcal/mol, respectively. There-

fore, for two or three double-bond systems the quantity $n \cdot (h(1) - h(e))$ can easily be of the order of 12–18 kcal/mol, a sizable chemical difference but one based entirely on the relatively small hydrogenation energy differences between the monoene and ethylene.

In the present work we compare some calculated energies for homomolecular differential bond separation and homodesmotic reactions and investigate the relationship given in eq. (13). As mentioned previously, both conventional *ab initio* as well as density functional calculations have been carried out.

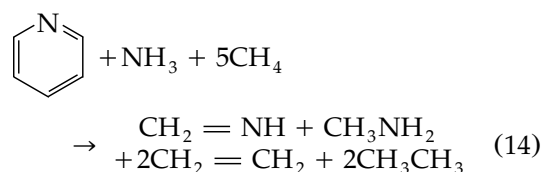
Details of Calculations

Energy difference (ΔE_{elect}) calculations were carried out using second order Møller–Plesset theory⁷ (MP2, frozen core) and density functional theory employing the Becke exchange functional²⁰ coupled with the correlation functional of Lee et al.²¹ (both gradient-corrected functionals), a density functional approach referred to here as BLYP and one that has yielded generally good results for energies, vibrational frequencies, and structures.^{22–25} All structures were optimized by each method using the 6-31G(d) basis set followed by single-point energy calculations at the 6-311G(d,p) level⁵; using conventional notation, energies were thus obtained at the mp2/6-311G(d,p)//mp2/6-31G(d) and BLYP/6-311G(d,p)//BLYP/6-31G(d) levels. For the three anions studied calculations were also performed with the diffuse-function-containing 6-311++G(d,p) basis on structures optimized at the 6-31+G(d) level.⁵ No rovibrational or translational energy corrections that would convert ΔE to ΔH were calculated. The GAUSSIAN 94 code²⁶ on the North Carolina Supercomputing Center's Cray Y-MP and T-90 platforms was employed in all calculations.

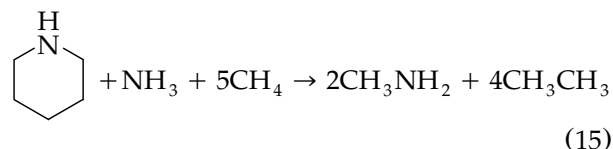
Results and Discussion

For systems in which heteroatoms are not formally involved in a double bond, energies were calculated according to the reaction schemes illustrated previously in eqs. (1) and (4)–(8). The situation for monocycles where a heteroatom is involved in multiple bonding is straightforward for the bond separation reactions such as, for example,

in pyridine

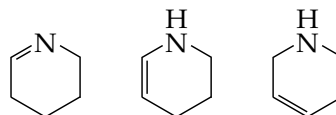


with a corresponding equation for piperidine

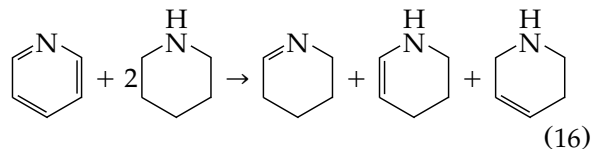


In this case, the hydrogenation energy $3h(e)$ in eq. (11) is replaced by $2h(e) + h(\text{CH}_2\text{NH}) \equiv 3h_{\text{eff}}(e)$ because of the formal double bond in pyridine involving nitrogen. This presents no real difficulties in practice, but does somewhat complicate the previous simpler interpretation, which involved only ethylene hydrogenation energies.

The homomolecular homodesmotic reaction is more involved in that there is no longer only a single monoene to consider, but rather three:

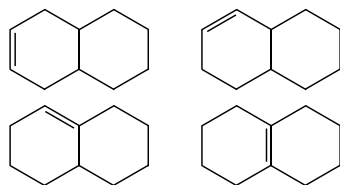


The proper "weighting" of the various monoenes is also unclear, but it would seem reasonable to treat each form equally, resulting in the reaction shown in eq. (16) which we have employed in our calculations here. Relating this reaction to hydrogenation reactions is now complicated by the need to consider the $h(1)$ terms for *each* of the monoene forms shown above.



We have not performed calculations on any polycyclic systems but mention them here for completeness. Polycyclic systems are again straightforward for bond separation reactions. For example, for naphthalene there is obviously only one fully unsaturated form and only one fully saturated form, and only ethylene hydrogenation reactions are involved when writing down the homomolecular differential bond separation reaction. But, again, the homomolecular homodesmotic reaction is more

complicated. There are now four forms of the monoene and a proper weighting for the reaction is not so apparent. We conclude from this that homomolecular differential bond separation reactions are more easily handled and may be preferred for polycyclic systems such as those illustrated above.



What we have suggested earlier and what we demonstrate in what follows is that, depending on the monoene involved, the homomolecular differential bond separation reaction energy is often simply related to that of the corresponding homomolecular homodesmotic reaction. But before we do that we want to emphasize that the homomolecular homodesmotic reaction is to be preferred when discussing cyclic conjugation, even though some ambiguities arise in treating heteronuclear and multiring systems. In the homomolecular homodesmotic reaction the same basic molecular structure is preserved, effects of strain should tend to cancel out where present, and no "extra" supporting molecules like ethylene and ethane or the simple hydrides need be involved.

Table I contains the results of our MP2 and BLYP calculations.²⁷ Several cases help reinforce the case for calculation of the conjugation energies from the homomolecular homodesmotic reaction rather than the differential bond separation reaction. Cyclopentadiene has an $H(2)$ value close to zero as we anticipate for this weakly conjugated system,²⁸ whereas the $\Delta B(2)$ value is about 18 kcal/mol. The cyclopentadienyl anion, which satisfies the Hückel $4n + 2$ rule, has an $H(2)$ value close to isoelectronic pyrrole, whereas the associated $B(2)$ and $\Delta B(2)$ values are very much larger. The cyclopentadienyl cation displays its antiaromatic character very well with a large and negative $H(2)$ value, but the $\Delta B(2)$ value is essentially zero. The B and ΔB values of benzene and pyridine are about the same, whereas the $H(3)$ values show benzene to have greater cyclic conjugation by about 6–8 kcal/mol, a difference one might expect based on the electronegativity difference effects of a nitrogen atom replacing one of the carbons in the six-membered ring.

The statistical analyses at the bottom of Table I comparing the MP2 and BLYP methods show that



they provide basically the same results. The MP2 energies are larger on average by 3–4 kcal/mol for the $B(n)$ and $\Delta B(n)$ terms, results seen in a previous investigation of bond separation energies.⁸ The two types of theoretical approaches are essentially statistically equivalent for the other energies. Because our earlier comparison⁸ of heats of formation showed that the BLYP density functional results match experiment better than MP2, we would probably choose to use the BLYP data first.

Table I also includes data for the three anions studied using basis sets with diffuse functions, that is, energies calculated with a 6-311 + G(d,p) basis from structures optimized at the 6-31 + G(d) level. While the use of diffuse functions for anions is generally desirable, here it appears to make only small changes to the calculated energy differences, a result likely caused by cancellation effects from the two sides of the reaction equations.

But, while the homomolecular homodesmotic reaction may be preferred, the previous discussion has shown that the homomolecular differential bond separation reaction energy is often simply related to that of the homomolecular homodesmotic energy, the difference between these two being the difference between the hydrogenation energy of the appropriate monoene and ethylene multiplied by the number of formal double bonds in the fully unsaturated system. When the monoenes are similar in character, the two types of reaction energies should be linearly related. For example, for the five-membered ring systems involving BH_2^- , CH_2 , NH , O , AlH_2^- , SiH_2 , PH , and S (see Table I for notation), the average (BLYP) difference between the two types of reactions is 8.6 kcal/mol with a standard deviation of 1.7 kcal/mol. For the six-membered rings involving B , CH , N , SiH , and P , the (BLYP) average is 5.8 kcal/mol with a standard deviation of 1.3 kcal/mol. These standard deviations are chemically rather small and likely well within the calculational noise level.



To illustrate the simple relationship that is often obtained between the $\Delta B(n)$ and $H(n)$ energies, we show in Figure 1 a plot of ΔB versus H (for the BLYP data) for the five- and six-membered rings (with the exception of the cyclopentadienyl anion and cation (*vide infra*)). Because the quantity $n \cdot (h(1) - h(e))$ is approximately the same for the two kinds of rings, a single straight line of unit slope and an intercept corresponding to the overall average of both types of rings (17.2 kcal/mol) may be drawn to emphasize the basic linear relation between the two types of reactions.

TABLE I. Reaction Energies (in kcal/mol) for Bond Separation Reactions Involving n Double Bonds ($B(n)$) and No Double Bonds ($B(0)$), the Differential Bond Separation Reactions ($\Delta B(n)$), Homodesmotic Reactions Involving n Double Bonds ($H(n)$), and the Normalized Difference between $\Delta B(n)$ and $H(n)$.^a

					
	$B(n)$	$B(0)$	$\Delta B(n)$	$H(n)$	$[\Delta B(n) - H(n)] / n$
A. Five-membered rings					
BH	5.73	−0.31	6.05	−19.08	12.56
	1.36	−4.13	5.50	−22.45	13.97
CH ⁺	−16.65	−15.07	−1.48	−56.77	27.65
	−16.45	−14.41	−2.05	−59.05	28.50
BH ₂ [−]	25.64 (29.82)	3.38 (3.94)	22.26 (25.88)	5.34 (3.16)	8.46 (11.36)
	23.84 (27.09)	−0.28 (−0.05)	24.12 (27.14)	3.21 (3.31)	10.45 (11.92)
CH ₂	20.03	2.94	17.09	3.21	6.94
	17.34	−0.39	17.73	2.80	7.46
CH [−]	96.54 (96.70)	13.12 (15.00)	83.42 (81.70)	27.71 (25.52)	27.85 (28.09)
	86.59 (85.06)	9.65 (10.97)	76.94 (74.10)	23.12 (23.35)	26.91 (25.37)
NH	53.73	8.91	44.82	25.18	9.82
	48.56	5.58	42.99	21.00	11.00
O	48.58	11.66	36.92	19.83	8.54
	43.61	8.46	35.14	15.47	9.84
AlH	9.50	−5.74	15.24	−6.06	10.65
	6.74	−8.71	15.45	−8.27	11.86
AlH ₂ [−]	17.26 (19.76)	−1.15 (−1.08)	18.42 (20.84)	1.40 (1.62)	8.51 (9.61)
	15.52 (17.04)	−4.63 (−4.98)	20.14 (22.02)	1.19 (1.66)	9.48 (10.18)
SiH ₂	10.74	−1.69	12.43	−1.17	6.80
	8.52	−5.24	13.76	−2.22	7.99
PH	24.93	6.62	18.30	6.62	5.84
	21.16	2.29	18.87	5.84	6.51
S	45.09	11.17	33.92	23.18	5.37
	37.32	6.23	31.10	18.74	6.18
B. Six-membered rings					
B	42.85	5.07	37.78	26.88	3.63
	37.19	−0.14	37.33	24.88	4.15
CH	68.23	11.54	56.69	41.46	5.07
	63.51	5.85	57.66	39.31	6.12
N	70.67	16.45	54.21	35.63	6.19
	65.89	10.80	55.10	30.79	8.10
SiH	53.75	4.21	49.55	36.59	4.32
	48.89	−1.49	50.38	35.31	5.02
P	64.22	11.91	52.31	41.27	3.68
	57.79	5.07	52.73	36.58	5.38
C. Some other molecules					
<i>Trans</i> -butadiene ^b					
	13.67	4.38	9.29	8.36	0.47
	14.46	2.15	12.32	8.98	1.67
Allene	−2.81	2.21	−5.02	−10.42	2.70
	0.36	1.12	−0.76	−8.31	3.78
Cyclobutadiene	−52.28	−19.40	−32.88	−33.72	0.42
	−51.04	−19.40	−31.64	−34.41	1.39

(Continued)

TABLE I.
(continued)

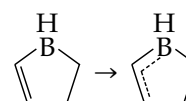
					
	$B(n)$	$B(0)$	$\Delta B(n)$	$H(n)$	$[\Delta B(n) - H(n)] / n$
Cyclohexatriene					
	47.81	11.54	36.27	21.05	5.07
	43.92	5.85	38.07	19.72	6.12
MP2-BLYP differences					
\bar{x}	3.72	3.73	-0.00	2.11	-1.02
σ	3.27	1.74	2.59	1.89	0.59

^a The X-substituent for the ring systems is indicated separately for the five- and six-membered rings. The first row of data for each molecule are the MP2 results, and the second row those for the BLYP density functional calculations. Results using diffuse functions for the anions are shown in parentheses. Statistics regarding the differences between the MP2 and BLYP results are shown on the bottom of each column.

^b The extended or trans form of 1-butene was used for the $H(n)$ calculations rather than the more stable cis form to maintain the similarity of the structure on each side of the homodesmotic reaction equation.

The points for the five-membered BH and AlH systems are also included in Figure 1. These two molecules are basically planar about B (and Al) and may be described as being sp^2 hybridized with an empty p π -orbital able to conjugate with the adjacent carbon-carbon double bond; this situation is indicated schematically below for

dihydroborole



This extra conjugation stabilizes the monoene and leads to a decrease of its (negative) hydrogenation energy and, therefore, an increase in the (positive) difference ($h(1) - h(e)$). It is because these molecules have conjugated monoenes that they tend to fall off the straight line in the figure. When this conjugation is prevented by forming the BH_2^- and AlH_2^- molecules, the resulting behavior is like the other systems shown.

While the conjugation in the BH and AlH monoenes is relatively weak, it is much stronger for the cyclopentadienyl cation and anion. The cation is antiaromatic (disobeys the $4n + 2$ rule) and shows a large negative $H(n)$ while the anion is aromatic (obeys the $4n + 2$ rule) and has a large positive $H(n)$. Both monoenes are conjugated in the same sense as BH above, but now the conjugation is much stronger because the three-atom system involved is allylic, that is, composed of all carbon atoms. In both systems the degree of extra conjugation is approximately the same as shown by these molecules having essentially the same value for $(h(1) - h(e))/n$ of about 28 kcal/mol. This result can be rationalized in terms of simple π molecular orbital theory by recognizing the fact that the three-atom bonding π -orbital is doubly occupied in each case, whereas whether the non-

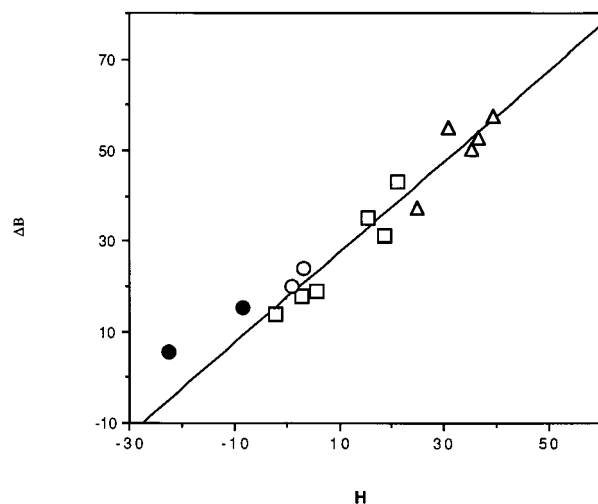


FIGURE 1. A plot of $\Delta B(n)$ versus $H(n)$ BLYP density functional theory energies (kcal/mol) for the five-membered rings involving CH_2 , NH , O , SiH_2 , PH , S (open squares), BH_2^- , and AlH_2^- (open circles); BH and AlH (closed circles); and the six-membered rings involving B , CH , N , SiH , and P (open triangles). See Table I for notation. The straight line is a line of unit slope with an intercept of 17.2 kcal/mol (see text).

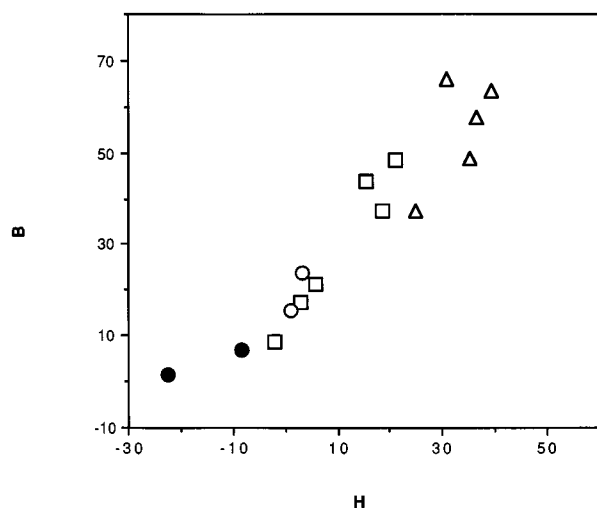


FIGURE 2. A plot of $B(n)$ versus $H(n)$ BLYP density functional theory energies (kcal/mol). The molecular systems and notation are the same as in Figure 1.

bonding π -orbital is filled (in the anion) or empty (in the cation) makes little difference to the overall π energy.

In our earlier work⁸ on bond separation energies we showed that this approach to determining cyclic conjugation energies correlated reasonably well with other approaches, including the homomolecular homodesmotic results of Schleyer et al.¹⁵ Figure 2 shows a plot of $B(n)$ itself versus $H(n)$ using the same BLYP data as in Figure 1. It can be seen that the two quantities are clearly correlated, but there is greater scatter of data than when $\Delta B(n)$ is plotted versus $H(n)$ (Fig. 1).

Table I also contains data for *trans*-butadiene, allene, cyclobutadiene, and cyclohexatriene, the latter hypothetical molecule formed by forcing the six-membered ring to have ethanelike single bonds alternating with ethenelike double bonds obtained from optimizations on ethane and ethene, respectively. As expected, *trans*-butadiene shows a small degree of conjugation, allene is somewhat destabilized in this regard with both $\Delta B(n)$ and $H(n)$ exhibiting negative values, and cyclobutadiene is strongly antiaromatic. Cyclohexatriene shows a relatively strong degree of cyclic conjugation stability and has $\Delta B(n)$ and $H(n)$ values that are approximately 60% of those for benzene itself! Its values of $(h(1) - h(e))/n$ are equal to those for benzene because the monoene involved is the same. For cyclobutadiene, the value for $(h(1) - h(e))/n$ is virtually zero, consistent with the idea that strain energies must cancel each other in the hydrogenation

reaction involving the strained cyclobutene and cyclobutane rings.

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References

1. L. Pauling, *The Nature of the Chemical Bond*, 2nd Ed., Cornell University Press, Ithaca, NY, 1948.
2. V. I. Minkin, M. N. Glukhovtsev, and B. Ya Simkin, *Aromaticity and Antiaromaticity*, John Wiley & Sons, New York, 1994.
3. G. W. Wheland, *Resonance in Organic Chemistry*, John Wiley & Sons, New York, 1955, ch. 3.
4. W. J. Hehre, R. Ditchfield, L. Radom and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).
5. W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley & Sons, New York, 1986.
6. P. George, C. W. Bock, and M. Trachtman, *Tetrahed. Lett.*, **26**, 5667 (1985).
7. C. Møller, and M. S. Plesset, *Phys. Rev.*, **46**, 618 (1934).
8. D. B. Chesnut, *J. Comput. Chem.*, **16**, 1227 (1995). In this article, a reviewer pointed out that there are problems of uniqueness of the classical structure for certain molecules. For example, the adjacent nitrogen atoms in the conjugated six-membered ring of pyridazine pose the problem of whether to bond separate these species as diimine and two methyl amines or as hydrazine and two methyl amines or as hydrazine and two methylene imines. This ambiguity appears not to have been discussed in the literature.
9. P. George, M. Trachtman, C. W. Boch, and A. M. Brett, *Theor. Chim. Acta*, **38**, 121 (1975). While George et al. defined this type of reaction as "homodesmotic," the term "homodesmic" has also been used in the literature.
10. L. Nyulászi, P. Várnai, S. Krill, and M. Kegitz, *J. Chem. Soc. Perkin Trans.*, **2**, 315 (1995).
11. L. Nyulászi, P. Várnai, and T. Veszprémi, *J. Mol. Struct. (Theochem)*, **358**, 55 (1995).
12. B. A. Hess, Jr. and L. J. Schaad, *J. Am. Chem. Soc.*, **105**, 7500 (1983).
13. G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **58**, 146 (1936).
14. G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **58**, 137 (1936).
15. P. v. R. Schleyer, P. K. Freeman, H. Jiao, and B. Goldfuss, *Angew. Chem. Int. Ed. Engl.*, **34**, 337 (1995).
16. One of the referees suggested the terminology "homomolecular isodesmic" for this type of reaction. The reaction certainly is isodesmic, but we feel that including the modifying term "homodesmotic" better reminds us of its origin.

17. M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).
18. B. Y. Simkin, V. I. Minkin, and M. N. Glukhovtsev, *Adv. Heterocycl. Chem.*, **56**, 303 (1993).
19. J. B. Pedley, R. D. Naylor, and S. P. Kirby, *Thermochemical Data of Organic Compounds, 2nd Ed.*, Chapman & Hall, New York, 1986.
20. A. D. Becke, *Phys. Rev. A*, **38**, 3098 (1988).
21. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, **37**, 785 (1988).
22. P. M. W. Gill, P. M. W. Johnson, J. A. Pople, and M. J. Frisch, *Chem. Phys. Letts.*, **197**, 499 (1992).
23. P. M. W. Gill, B. G. Johnson, J. A. Pople, and M. J. Frisch, *Int. J. Quantum Chem. Symp.*, **26**, 319 (1992).
24. C. W. Murray, G. J. Laming, N. C. Handy, and R. D. Amos, *Chem. Phys. Lett.*, **199**, 551 (1992).
25. B. G. Johnson, P. M. W. Gill, and J. A. Pople, *J. Chem. Phys.*, **98**, 5612 (1993).
26. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *GAUSSIAN 94, Revision C.3*, Gaussian, Inc., Pittsburgh, PA, 1995.
27. Our MP2 results for the five-membered rings are in good agreement with the calculations of Schleyer et al.,¹⁵ and are some 8.5 kcal/mol higher on average than the results of Nyulaszi et al.¹¹ who used the non-homomolecular homodesmotic reaction approach with zero-point energy corrections.
28. The question of the potential aromaticity of cyclopentadiene has been discussed by H. Jiao and P. v. R. Schleyer, *J. Chem. Soc. Faraday Trans.*, **90**, 1559 (1994).